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Sugar reduction in musts with nanofiltration membranes to obtain low alcohol-content wines

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ABSTRACT

Our aim here is to study the sugar reduction in musts to obtain wines with a slight alcohol reduction by nanofiltration. Specifically, sugar reduction is achieved by two successive nanofiltration steps. To test the method, we have worked with two types of musts: a white must from *Verdejo* grapes and a red one from *Tinta de Toro* grapes. The musts obtained from the nanofiltration treatment have been mixed with untreated must or with the retentate of the first nanofiltration stage in a proportion adequate to reduce the alcohol content of the resulting wines by 2°.

To verify the effectiveness of the process, each of these musts has been fermented along with an untreated control sample of the same must. The alcohol reduction in the wines has been satisfactory. However, a slight loss in the color and aroma of some compounds has been detected.

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1. Introduction

One of the most popular drinks in the world is wine, mainly in Mediterranean countries such as Spain, France or Italy, which not casually are the most important producers of wine in the world [1].

Wine is a complex alcoholic beverage with more than 800 organic compounds [2] which contribute to the flavor and their specific aromas. This means that any wine process must optimize the aroma, the flavor and minimize the formation of non-desired characteristics (i.e. plastic flavor) [3,4]. In the last years, the alcohol content tended to increase, due to different factors. One of them is the sugar increase in must, attributed to the climate change. A premature winemaking should result in a loss of other very relevant qualities linked to ripeness. Actually there is a growing demand, by consumers, of more powerful and full flavored wines that are achieved with greater maturity of the grapes, both skin and seeds. This means that producers struggle to achieve the same levels of phenolic ripeness and tannic characteristics without an increase in alcohol content. But, at the same time, consumers demand more and more reduced alcohol beverages as a result of health and social concerns (i.e. traffic penalties) [5].

Wine producers have started to use dealcoholization process or methods to produce low alcohol-content wine. The most used method in the industry is the spinning cone column (SCC). SCCs are used in the food industry for the separation of volatile components from liquids and slurries [6–9]. This process requires several steps to remove first the wine aromas and afterwards alcohol and finally the aromas are added back to the dealcoholized wine. This is a long and expensive process. Other techniques have been used to reduce the alcohol content of wine: aerobic yeasts [10], thermal and distillation process, as evaporators, distillation columns or freeze concentration; or extraction processes [11].

Membrane filtration has been applied to wine for a long time: ultrafiltration (UF) to clarify white wine from grape must [12], sugar concentration using nanofiltration (NF) [13] and reverse osmosis (RO) [14] in musts. Reverse osmosis is also used to reduce alcohol in wines [15], but the problem is that RO membranes are permeable to both alcohol and water, and after the filtration it is necessary to add water again to the dealcoholized wine which creates legal problems in some countries where the addition of water is prohibited. Of course the permeated water could be separated from alcohol to add this water back to wine. This should be, in principle, allowed because this water is coming from the same wine. Other membrane processes, such as dialysis [16,17] or pervaporation [18] or vacuum membrane distillation [19], are being used to get low-alcohol wine or beer.

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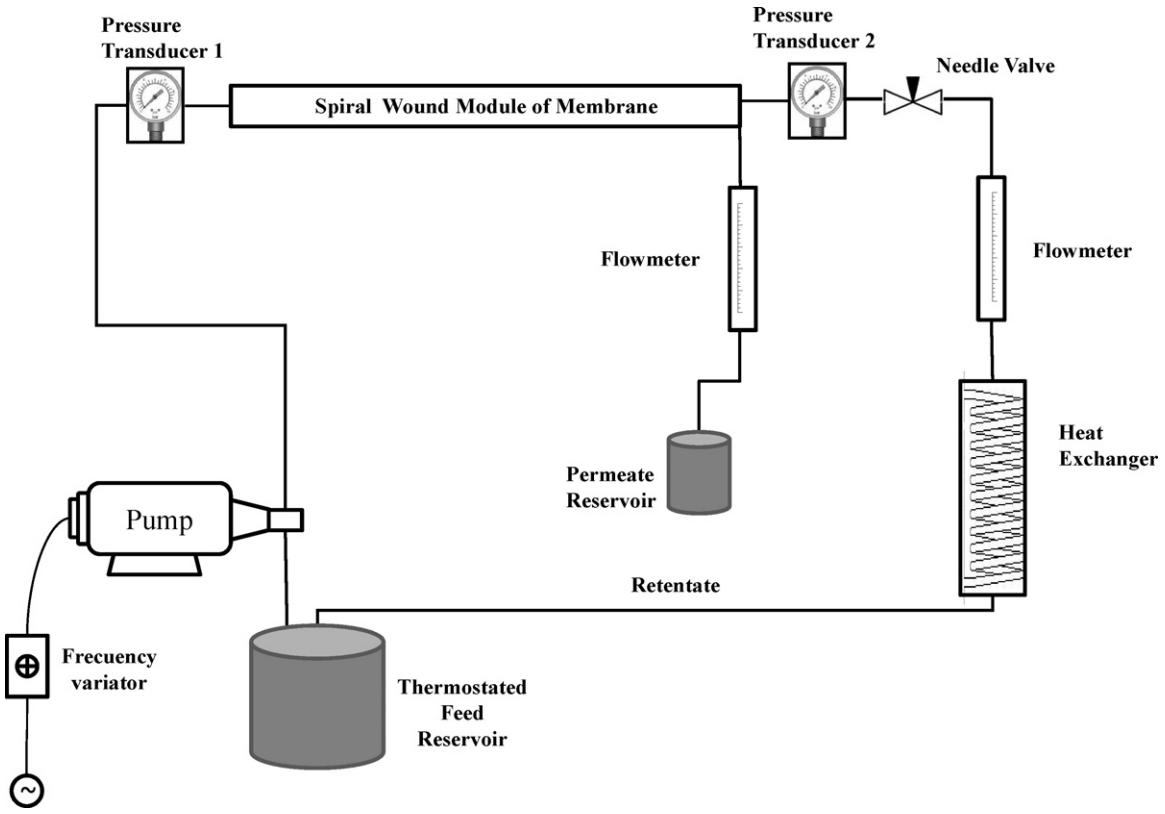

Fig. 1. Diagram of the experimental setup used in the process of musts nanofiltration.

Here we obtain low-alcohol wine by sugar control in winemaking. For this purpose, nanofiltration membranes have been used to reduce sugar concentration in must, previously to the fermentation. The idea of reducing the resulting content of alcohol in wine by reducing sugar in the must by membrane processes is not new [20–22]. In this work, we will use two-step nanofiltration in order to simplify the process. This will be tested by treating the musts coming from two varieties of grapes, a white one (*Verdejo*) and a red one (*Tinta de Toro*).

Verdejo is one of the best Spanish white grape varieties. It is mainly grown in the Denomination of Origin Rueda (Valladolid), in the Autonomous Community of Castilla y León. It can be also found in Portugal. *Verdejo* wines have a unique flavor, with a hint of scrub herbs, a fruity touch and an excellent level of acidity. The extract, a key factor when assessing the personality of great white wines, is perceived through its volume and its characteristic bitter touch, which leaves a glint of originality in the mouth, accompanied by a rich fruity expression. These wines are harmonious, and their aftertaste induces to go on drinking.

Tinta de Toro grapes are a variety of Tempranillo grape grown in the Denomination of Origin Toro in Castilla y Leon too. Tempranillo grapes are the most cultivated grapes in Spain. They are also grown in Portugal, Francia, Argentina and United States. *Tinta de Toro* wines can be consumed young (without oak), but most of them are aged for different periods of time in oak barrels. *Tinta de Toro* young wines have intense cherry pink color and hints of blue, indigo, violet and purple in the fine layer, with very important primary aromas of wild red fruits and important tannic acid component that rounds off with time, especially with the ageing in barrel. The wines aged in barrel ("crianza wines") have red cherry color in the top layer and a great intensity of color with violet shades in the fine layer. Primary and secondary aromas appear in the olfactory phase with a great balance between wine and wood. These wines are well structured, with a compact body and a lasting spice and fragrant finish.

After nanofiltration of these musts and once the fermentation is completed, a thorough analysis has been made to consider all the possible changes in the wine characteristics: chemical constituents, since the understanding of the chemical nature of the wine could help to improve the method [23]; and volatile composition, because of the importance of the wine aroma, which is one of the main factors contributing to the quality of the wine [24–26].

2. Materials and methods

2.1. Membrane equipment

The experimental set-up used for must filtration is shown in Fig. 1. It consists of a feed vessel, with a cryogenic unit to assure the conservation of the must at low temperature (<10 °C), avoiding the fermentation; a magnetic coupled external gear pump, Tuthill® TXS2; a spiral wound module of nanofiltration HL Series Thin Film Membrane (reference HL2540FM) made and commercialized by GE Water & Process Technologies (Cutoff retention 98% for $MgSO_4$; water permeability from 0.94×10^{-11} to 4.55×10^{-11} m/Pa s); pressure gauges to measure the inlet and outlet pressures in the membrane module; and flowmeters for retentate and permeate flux rate measurements. The module has a membrane area of 2.5 m^2 with a channel length $L = 1.016$ m, wetted perimeter $P = 4.92$ m, cross-section available for the flow $A = 1.87 \times 10^{-3}$ m^2.

Previously to the choice of that membrane, a series of membranes in flat configuration, from GE Water & Process Technologies, were tested using isomolecular mixtures of glucose and fructose at a total concentration of 249.58 g/L (which is what is usually found in musts) and commercial musts. They are UF-GH, NF-HL, NF-DL and NF-DK; among the membranes studied by us, NF-HL seemed

Table 1
Oenological parameters for the musts before the nanofiltration process.

Must	pH	A.T. (g/L)	MH2 (g/L)	TH2 (g/L)	Sugar[a] (g/L)	Glucose	Fructose	G/F	Sugar[b] (g/L)	Probable Alcoholic degree[c] %vol	SO_2L (mg/L)	SO_2T (mg/L)	Potassium (mg/L)
Tinta de Toro Initial	3.76	3.91	4.4	2.3	247.7	116.3	155.8	0.7	272.1	14.2	32	61	1790
Tinta de Toro Pre-filtered	3.76	3.87	4.0	1.9	249.7	87.0	178.0	0.5	265.0	14.3	29	53	1780
Tinta de Toro (control)	3.76	3.78	3.8	2.1	244.0	135.0	128.5	1.1	263.5	14.0	29	51	1820
Verdejo Initial	3.42	4.93	4.5	2.7	208.0	–	–	–	–	11.9	29	81	1250
Verdejo prefiltered and used as control	3.37	4.79	4.0	2.8	209.0	109.0	94.0	1.2	203	12.0	43	49	1090

A.T. = total acidity, SO2L = free sulfurous oxide, SO2T = total sulfurous oxide, G/F = glucose/fructose ratio, MH2 = malic acid; TH2 = tartaric acid.
[a] Elaborated from the refractometer tables of equivalence brix-molarity [29].
[b] Addition of glucose and fructose as obtained by the enzymatic method.
[c] Estimated from tables of the alcoholic degree to be expected from the sugar content of must [29]

to be the adequate one as far as it gives a relatively low moderate retention of low molecular weight (LMW) compounds with a very high permeability. Results have been reported previously [27].

Before using the HL module, it must be rinsed with filtrated, distilled and de-ionized (Milli-Q quality) water for 2 h to remove the preserving solution. This was done at 25 °C, at 10 bar and with a flow of 0.5 L/min. After that, to condition the module, Milli-Q water was filtered during 2 h more at the same conditions of pressure, flow and temperature. Water permeabilities were measured after and before all filtrations and cleaning steps.

2.2. Musts

As already mentioned, two different musts have been used:

1. *The Verdejo white must*: Initial must was obtained using the traditional white must production method: after the destemming, crushing, sulphiting and pressing processes, pectinolytic enzymes were added to the resulting must to enhance first clarification. Once the must had been cleared, a part of the must was filtered through 0.8 μm plates in order to ensure optimum must clarity and to prevent rapid membrane fouling, thereby facilitating the filtering process. 30 L was used, with a sugar concentration, measured by refractometry, of 209 g/L and a turbidity of 9.5 NTU.
2. *The Tinta de Toro red must*: In this case, the part of the must whose sugar content was reduced was the first must obtained by drawing off. This process is carried out as soon as possible following destemming, crushing and sulphiting, in order to reduce the presence of phenolic compounds in the must to a minimum. The must was then filtered first with 3 μm plates and then with 0.8 μm plates in order to limit turbidity. In this case, the solid parts (which is called crushed mass and consists in the grape skins, seeds and so on) were cold-stored in airtight stainless steel tanks for addition to musts and to be fermented after nanofiltration. 30 L was used, with a sugar concentration, measured by refractometry, of 244 g/L and a turbidity of 3.6 NTU.

The addition of sulfur dioxide serves as an antiseptic and antioxidant, protecting wine from spoilage by bacteria and oxidation. It also helps to keep volatile acidity at desirable levels. In order to prevent possible oxidation, the prefermentative dose is set to the maximum recommended value: i.e. 50 mg/L approximately [28]. The composition of the original musts and its variation by the pre-filtering process through plate-filters is shown in Table 1. The difference between the pre-filtered musts and those used as control ones for the NF step is due to the time course from the plate-filtering day to the nanofiltration day. It is clear that must composition does not change significantly during plate-filtering.

2.3. Procedure

White must was kept at 3 °C during filtration. The operation conditions were 24 bar of pressure (averaged along the module with pressure drops of 1 bar approximately) and 1 L/min of recirculation flow rate. If the inter-membrane channel dimensions inside the module (that have been given in Section 2.1) are taken into account the tangential velocity in the module exit is 9×10^{-3} m/s. The total sugar concentrations (glucose plus fructose), both in the permeate and in the retentate, have been determined by refractometry every 30 min and the turbidity every hour. The flow in the permeate solution was measured every 30 min.

The red must was kept at 6 °C. The operation conditions were an average pressure of 24 bars and recirculation flow rate of 1.5 L/min at the module exit, which supposes a tangential velocity in the channel exit of 13.5×10^{-3} m/s. The total sugar concentration, in both permeate and retentate, turbidity and flow were measured every hour. In this case, due to the high content of total solids of the red wines, along with refractometry, polarimetry has also been used to determine the sugar concentration.

The differences in temperature and recirculation flow are due to the higher viscosity and thus to the more elevated friction and resistance to pumping shown by the red must. In both cases the volume filtered and retained in each filtration step are shown in Table 2.

For both musts, the way tested here as a possible method to reduce their sugar content consists in a double filtration in the following steps:

- Firstly the untreated must (T) is filtered to get a low volume of sugar rich retentate (R1) and a permeate with a medium sugar content (P1).
- After that, the membrane is rinsed with tap water during 2 h and with Milli-Q water during 1 h.
- Then, the first permeate (P1) is filtered through the same membrane until the viscosity and the osmotic pressure of the retentate do not allow any ulterior reduction of the retentate volume. This process provides a retentate (R2) with a high sugar content and a second permeate (P2) with a low sugar content.

Table 2
Filtration volumes for the musts in the nanofiltration process.

	V_{White} (L)	V_{Red} (L)
T	30	30
P1	14	12
R1	16	18
P2	12	10
R2	2	2

Finally, in the case of white musts

- The second permeate (P2) should be mixed with the first retentate (R1) or with the untreated or control must, in the suitable proportions to produce the intended moderate reduction in the alcohol degree of the final wine retaining the specific character linked to the high molecular weight components.
- Then both the mixtures R1 + T and R1 + P2 undergo the alcoholic fermentation

While for the red musts

- The second permeate (P2), the first retentate (R1) and the control must (T) with corresponding amount of crushed mass go through the alcoholic fermentation.
- Afterwards the fermented P2, R1 and T are mixed as R1 + T and R1 + P2 and then suffer the second or malolactic fermentation.

After that the resulting wines were analyzed attending to their chemical composition and their organoleptic properties. It is worth noting that several alcohol degree reductions have been obtained. To test the repeatability, two different fermentation containers (a and b) have been obtained for the same mixture.

The performance of the process has been determined by measuring the resulting permeate flux rate as a function of time, at constant conditions of pressure and recirculation flux [30]. The concentration measure of permeate and retentate has allowed us to determine the time evolution of the observed retention of the system, R_{obs}.

$$R_{obs}(t) = 1 - \frac{c_p}{c_o} \tag{1}$$

where c_p is the permeate concentration and c_o is the concentration of the feed. Membrane efficiency has been evaluated by determining the true retention, R, which is calculated through the following equation, as a time function [31,32]:

$$R(t) = 1 - \frac{c_p}{c_m} \tag{2}$$

where c_m is the concentration just in contact with the membrane which is bigger than the input concentration due to the accumulation of solute resulting from concentration polarization.

The true retention of the membrane has been evaluated according to the film-layer theory and without taking into account the effects of osmotic pressure or fouling. To compute the true retention, defined in Eq. (2), we need to calculate the concentration on the membrane surface, C_m. To do this, the Film Theory is used to correlate the feed concentration, C_0, with that on the surface of the membrane, C_m [33]:

$$C_m = C_p + (C_0 - C_p)\exp\left(\frac{J_V}{K_m}\right) \tag{5}$$

where K_m is the mass transfer coefficient, which can be evaluated using the Graez-Lévêque equation that, for laminar regime, states that the Sherwood number, Sh, can be written in terms of the Reynolds, Re, and Schmidt, Sc, numbers as:

$$Sh = 1.85\left(\frac{d_h}{L}Re \cdot Sc\right)^{1/3} \tag{6}$$

where d_h is the hydraulic diameter and L is the channel length, with

$$d_h = \frac{4A}{P} \tag{7}$$

$$\mathrm{Sh} = \frac{K_m d_h}{D_\infty} \tag{8}$$

Table 3
Summary of the methods used for the determination of the more significant oenological parameters for our musts and wines.

Property	Method
Glucose and fructose	Enzymatic method
Total sugar	Refractometry and polarimetry
Density	Brix degree for musts and densitometry for wines.
pH	pH-meter
Total acidity	Acid–base titration
SO_2	Iodometry
Alcohol degree	Distillation
Malic acid	Enzymatic method
Tartaric acid	Colorimetric method
Potassium	Atomic absorption spectroscopy
Total polyphenols	UV/Vis spectrophotometry
Anthocyanins	UV/Vis spectrophotometry
Tartaric esters	UV/Vis spectrophotometry
Color	UV/Vis spectrophotometry
Volatile compounds	Gas chromatography after extraction

$$Re = \frac{v\rho d_h}{\eta} \tag{9}$$

$$Sc = \frac{\eta}{\rho D_\infty} \tag{10}$$

where A is the transversal area of the channel; P is the transversal perimeter of the channel; giving an hydraulic diameter $d_h = 1.52 \times 10^{-3}$ m; v is the mean velocity inside the channel; ρ is the density 0.997 kg/L; η is the viscosity 8.9×10^{-4} Pa s; D_∞ is the diffusion coefficient of sugar 6.77×10^{-10} m^2/s. It is worth noting that v in Re is the average velocity along the channel that changes with J_V.

2.4. Cleaning

After must filtration, an important reduction has been observed in permeability, due to the fouling of the module. In order to reduce the fouling, the module has undergone a series of cleaning processes after each filtration experiment (i.e. after each must had passed the two nanofiltration steps). All the procedures were performed at 25 °C, under transmembrane pressures of 8 bar and with a recirculation flow on through the feed channel of 5 L/min.

- Rinsing with Milli-Q water during 60 min and permeability measurement.
- After this, a solution of 0.1% of sodium dodecyl sulfate [34] was used to clean the membrane module during 60 min at. This reduces the surface tension of the liquid, making easier to remove the dirt. pH was adjusted to 9 with NaOH and HCl during this cleaning step, according to the membrane manufacturers' specifications.
- Once more, rinsing with Milli-Q water during 60 min and permeability measurement.
- Storage in phenol solution, with pH 6

2.5. Must and wine analysis

In order to analyze the possible changes in the properties of must after filtration and the reduced alcohol degree wines obtained, a complete analysis of them has been made. The oenological parameters analyzed were determined according to the Organisation Internationale de la Vigne et du Vin (OIV) methods [35]. Table 3 summarizes the main techniques used.

The volatile compounds were isolated from wine by liquid-liquid extraction following the method described by Moio et al. [36]. Two hundred and fifty millilitres of wine, 5 mL of dichloromethane and 50 μL of an internal standard solution (2-octanol of 1000 μg/L) were introduced in a special flask in which oxygen had been previ-

Table 4
Hydraulic permeability of the nanofiltration membrane, both initially and after several processes of filtration and sodium dodecyl sulfate cleaning.

Process	Before filtration	After *Verdejo* filtration	After 1st cleaning	After *Tinta de Toro* filtration	After 2nd cleaning
L_p (10^{-13} m/Pa s)	193	125	153	157	158

ously removed by nitrogen. The flask was placed in an ice bath and stirred at 150 rpm for 3 h. Finally, organic phase was kept and stored at −80 °C until analysis. Each sample was extracted twice. Volatile compounds were analyzed, according to the method proposed by Ortega-Heras et al. [2], using gas chromatography.

3. Results and discussion

3.1. Nanofiltration processes

As mentioned, water permeability was measured before and after every use (filtration or cleaning process). This has allowed us to determine the loss of permeability due to fouling during the must filtration and the recovery after the cleaning process. Results are presented in Table 4. The water permeability obtained is within the range given by the manufacturers. It can be noticed that after nanofiltration of white must, water permeability was reduced by 35% and there is a slight recovery after the cleaning process, without reaching the original value of the brand new membrane (there is a final reduction of 20% over the original permeability). After filtration of red must, the permeability loss is almost negligible when compared with the permeability of departure and there is no recovery after the subsequent cleaning process.

Fig. 2 presents the kinetics of the flow of must. Fig. 2a and b compare how the flux of must falls in terms of the initial water flux (J_V/J_{Vw}) versus time, for the two musts (White and Red) and for the two consecutive filtration steps. It can be seen that the flux decrease is more significative in the case of the red musts than in the white ones. This decrease could be expected since there are several factors that promote this process [37,38]:

- The osmotic pressure increase due to the increment of the concentration of small molecules on the membrane surface (C_m) and due to the increment of their concentration in the retentate (C_o).
- Thickening of the gel layer on the membrane surface due to the rise of the concentration of big molecules and colloids on the membrane surface (C_m).
- Increase in the viscosity of the fluid that goes through the membrane pores.

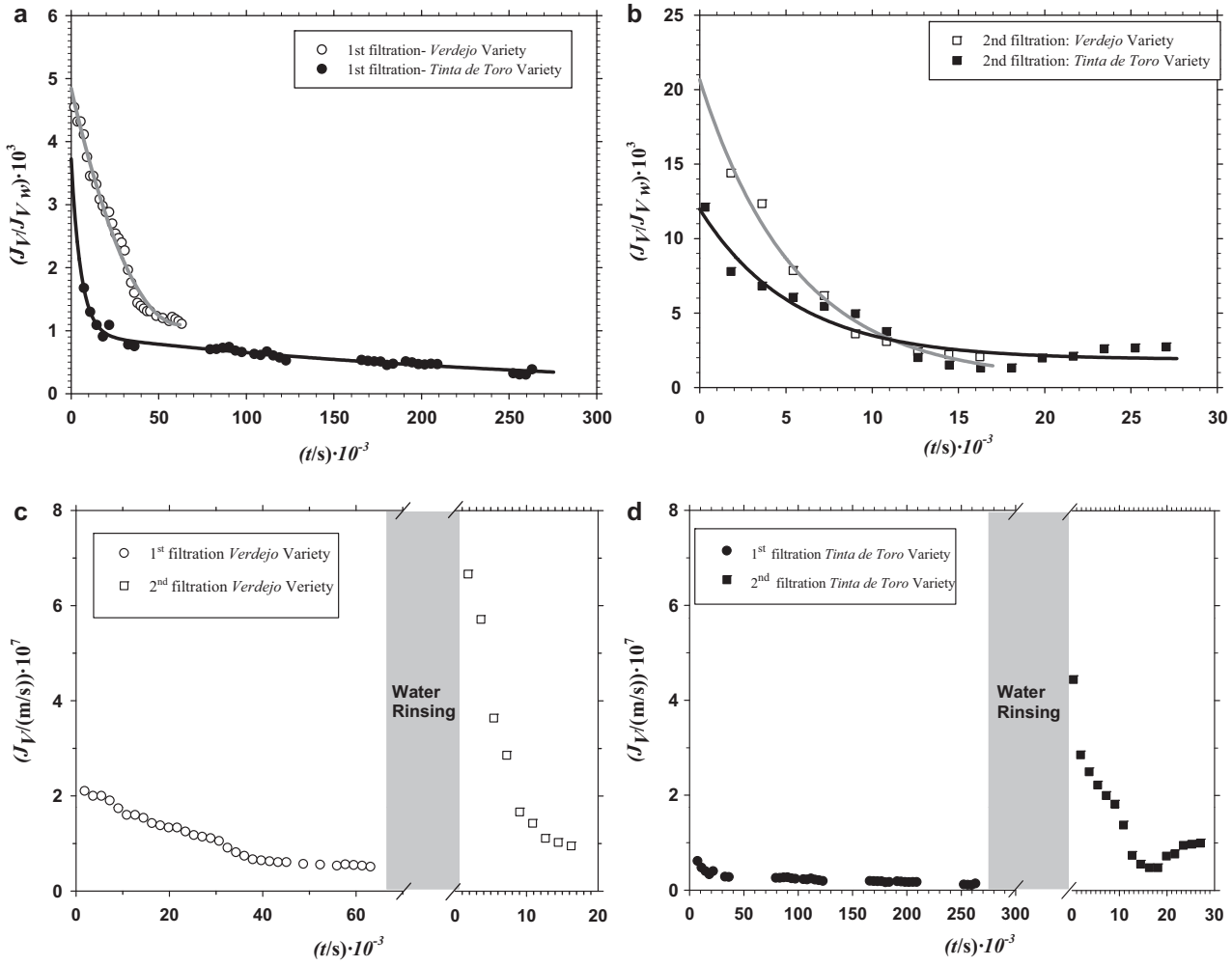

Fig. 2. Flux decay kinetic versus time. (a and b) Normalized flux decay with the water flux of the membrane before nanofiltration process ($J_{Vw} = 4.63 \times 10^{-5}$ m/s before the white wine filtration and $J_{Vw} = 3.67 \times 10^{-5}$ m/s before the red wine filtration), and (c and d) sequential representation of both filtration processes for each must.

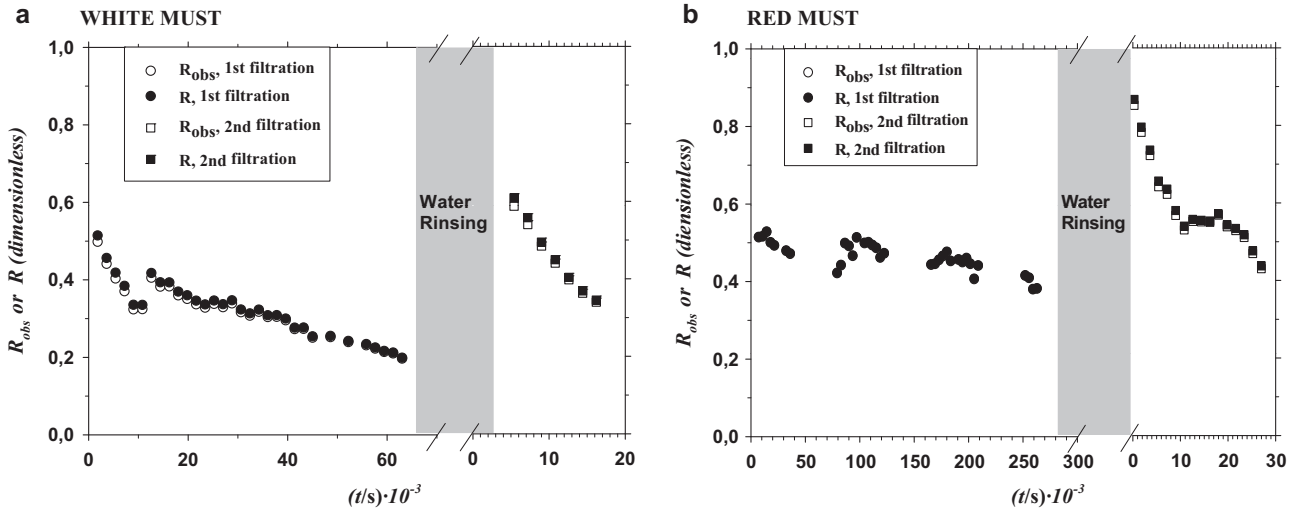

Fig. 3. Sequential representation of both observed and true retention for the nanofiltration processes: (a) white must and (b) red must.

- Fouling due to the reversible or irreversible adhesion of the molecules on the membrane surface or inside the pores.

When the overall process is taken into account the evolution of the volume flow can be written as:

$$J_V(t) = \frac{\Delta P - \Delta\pi(t)}{\eta(t) R_{sys}(t)} \quad (3)$$

where Δp is the applied pressure gradient, $\Delta\pi(t)$ is the osmotic pressure gradient which depends on the concentration difference between the both sides of the membrane, $\eta(t)$ is the viscosity of the solution and, $R_{sys}(t)$ is the system resistance, which is the addition of several contributions as:

$$R_{sys}(t) = R_m + R_g(t) + R_f(t) \quad (4)$$

The addends are the resistance of the whole membrane, R_m; the resistance of the gel layer, $R_g(t)$; and the resistance due to the fouling by molecules adsorption on the membrane (reversible or irreversible), $R_f(t)$ [39].

The importance of all these processes is increased with time. The first one can be modeled easily using the osmotic pressure model. The second and third processes can be understood using the gel layer model with variable feed concentration and increasing viscosity. The fourth process can be modeled with different kinetic mechanisms. These can appear simultaneously although in different proportions throughout the process [37,40,41]:

- Pore blocking that appears when molecules, with a size similar to the pore radius, block it and make it useless for the flux, decreasing the permeability.
- Adsorption on the pore walls that reduces the pore radius and thus the flux. In this case it appears an increasing rejection for molecules with the appropriate size; i.e. bigger than the new reduced pore radius. This means that the threshold molecular size of rejection decreases.
- Surface adsorption and accumulation in a layer on the surface of the membrane to form what is customarily called a "cake". This cake plays the role of a pseudo-membrane that changes both the permeability and the selectivity properties. This layer is normally built up from molecules that are bigger than the pore size with a contribution of the small ones as well. It differs from the concentration-polarization gel layer in the irreversible character of the cake which is only eliminated by cleaning as is the case with all the fouling mechanisms described.

The contribution of the osmotic pressure effect should be similar for both musts, white and red, because the concentration of small molecules (mineral salts, sugars, organic acids and other small molecules) is similar in both cases, as shown in Table 1 if we average the concentration of these compounds for both musts. This fact is illustrated in Fig. 2b, which shows a very similar behavior for both musts in their second filtration. A dramatic decline appeared during the first filtration that can be attributed to larger molecules. The contribution of the gel layer, the increasing viscosity and the cake formation effects is much more significant in the case of red musts, because in them there is a much higher concentration of large molecules such as proteins and polyphenols (Fig. 2a). White musts show higher flows decreasing also more slowly than the corresponding flows for the red musts during the first filtration step, that thus ended before for white than for red musts. For the second filtration step, white musts presented also higher fluxes but decreasing faster than for the red musts leading to a more similar time span for this second filtration step.

The importance of fouling mechanism is shown in Fig. 2c and d where it is seen that because the first permeate (P1) has a smaller concentration of large molecules, the initial flow of the second filtration is higher than the initial one of the first filtration stage. In the second stage, the effect of osmotic flow is also reduced as far as the concentration of sugar and other substances of low molecular weight decreases after the first filtration step. As a consequence the time for the completion of second nanofiltration step is shorter than for the first one, for both musts.

All these processes cause changes in the membrane retention over time. In order to highlight this fact, the sugar concentration has been determined versus the permeation time for both permeate and retentate, at both stages and for both musts. As mentioned before, in the case of white musts, concentrations were measured by refractometry, whereas for the red ones, they have been measured by polarimetry, due to the interferences caused by the high solid content of red musts in the refractrometric results. Using Eq. (1), $R_o(t)$ has been determined. Fig. 3a and b show that there is a decline in retention that should have been expected due to the increase in the concentration of the retentate that produces an increase in the concentration polarization and osmotic pressure effects. Moreover, fouling also changes the retention conditions of the membrane because it causes a decrease in the flow with time and it is known that lower fluxes are associated with lower retentions. Note that retention is higher for *Tinta de Toro* must than for *Verdejo*.

Table 5a
White musts (*Verdejo*). Total sugar concentration, determined by different methods, glucose and fructose concentrations, glucose versus fructose ratio and the expected alcoholic degree estimated before fermentation. (T: control must, P1: first permeate, P2: second permeate, R1: first retentate, R2: second retentate).

Must	Sugar[a] (g/L)	Glucose (g/L)	Fructose (g/L)	G/F	Sugar[b] (g/L)	Probable alcoholic degree[c] (%vol)
T	209.0	109.0	94.0	1.2	203	12.0
P1	133.0	78.0	66.0	1.2	144	7.3
P2	95.0	61.0	51.0	1.2	112	5.0
R1	247.0	144.0	139.0	1.0	283	15.9
R2	268.0	141.0	128.0	1.1	269	15.5

[a] Elaborated from the refractometer tables of equivalence brix-molarity [29].
[b] Addition of glucose and fructose as obtained by the enzymatic method.
[c] Estimated from tables of the alcoholic degree to be expected from the sugar content of must [29].

Table 5b
Red musts (*Tinta de Toro*). Total sugar concentration, determined by different methods, glucose and fructose concentrations and glucose versus fructose concentrations ratio and the expected alcoholic degree estimated before fermentation. (T: control must, P1: first permeate, P2: second permeate, R1: first retentate, R2: second retentate).

Must	Sugar[a] (g/L)	Glucose (g/L)	Fructose (g/L)	G/F	Sugar[b] (g/L)	Sugar[c] (g/L)	Probable alcoholic degree[d] (%vol)
T	244.0	135.0	128.5	1.1	263.5	253.81	14.0
P1	146.0	81.0	75.0	1.1	156	159.90	8.4
P2	94.0	59.2	53.8	1.1	113	101.52	5.6
R1	294.0	149.0	157.0	0.9	306	329.95	16.8
R2	290.7	153.5	150.5	1.0	304	312.18	16.6

[a] Elaborated from the refractometer tables of equivalence brix-molarity [29].
[b] Addition of glucose and fructose as obtained by the enzymatic method.
[c] Addition of glucose and fructose as obtained by the polarimetric method.
[d] Estimated from tables of the alcoholic degree to be expected from the sugar content of must [29].

Fig. 3a and b show the results for the true retention $R(t)$ along with the corresponding $R_o(t)$ as commented. It can be noted that in both musts and filtration stages the difference between the true and observed retention is very small. This is because the effect of sugar on the formation of the gel layer is not important. Furthermore, by looking at the second stage, where much of the large molecules have been eliminated, R is not constant. This is because the effect of the osmotic pressure is the determining factor in this case.

3.2. Analysis of the filtrated musts

Recalling that the aim of this work is to get a small reduction in the alcohol content of wine using the permeate of the second filtration process and the retentate of the first filtration step, it is clearly essential to analyze the main characteristics of the obtained musts. To do this, the concentrations of the final products of the permeate and retentate have been studied, for each stage of the process. Given the large number of substances involved in the wine composition, we will classify them into three groups: sugars, other small molecular weight substances and polyphenols.

The fundamental objective is the sugar reduction in the final permeate, in such a way that an adequate mixing of it with the retentate of the initial process or with the untreated must could lead to must with an adequate reduction in sugar. The simplest method of determining the sugar content is from the index of refraction, where only a drop of the sample is required. Unfortunately, this method is interfered by the presence of other substances in wine, and involves some error, especially when the filtration is changing the balance of these other substances. The polarimetric method has less interference, but the accuracy is not high due to the opposed rotation of the polarization plane induced by the two main sugars appearing in wine. Finally, the enzymatic method allows us to determine the amount of glucose and fructose separately, with greater accuracy and it is recommended by the OIV.

Tables 5a and 5b show the results of the sugar determination for the untreated or control must and for the final permeate and retentate, after each process. With the errors inherent in each technique, it can be said that the results are similar for all the methods. In terms of classic oenological parameters, the application of membrane treatments merely modified the total sugar concentration of the initial must and therefore the probable alcohol contents to be reached after fermentation, as the glucose/fructose ratio found in the control must was equal to that found in the permeate, obtained after the second filtration step (P2). The alcoholic grade of the wine that would be obtained from the musts is presented in the last column of these tables. Note that in the case of the white musts after fermentation we would reduce the alcohol degree from 12° to as low as 5°, and for the red we should go from 14° to 5.6°. However, our goal is not to drastically reduce the alcoholic degree, but a small reduction as we have said it would be achieved by mixing the final permeate with the initial retentate or with the control must. In this way, it would regain other important substances in the winemaking process that have not passed to the final permeate.

For the sake of a quantification of the effectiveness of nanofiltration stages, the sugar reduction, r, has been determined for each stage, for the total process and referred to the control must:

$$r = 1 - \frac{c_p^t}{c_r^t} \tag{11}$$

where c_p^t is the concentration in the permeate tank and c_r^t is the concentration in the retentate one, once the process has been finished.

For these calculations, the concentrations determined by the enzymatic method (more accurate) have been used. Table 6 shows

Table 6
Sugar reduction in musts for different processes.

Process	White must (%)	Red must (%)
1st Process: $r = 1 - \frac{c_p^t(\mathrm{P1})}{c_r^t(\mathrm{R1})}$	49.1	49.0
2nd Process: $r = 1 - \frac{c_p^t(\mathrm{P2})}{c_r^t(\mathrm{R2})}$	58.4	62.8
Global process: $r = 1 - \frac{c_p^t(\mathrm{P2})}{c_r^t(\mathrm{R1})}$	60.4	63.1
For control must: $r = 1 - \frac{c_p^t(\mathrm{P2})}{c_r^t(\mathrm{T})}$	44.8	57.1

Table 7a
pH, acidity and substances of low molecular weight for the white musts (from *Verdejo* grapes).

Must	pH	A.T. (g/L)	MH2 (g/L)	TH2 (g/L)	Potassium (mg/L)
T	3.37	4.79	4.0	2.8	1090
P1	3.68	4.56	4.0	2.0	1030
P2	3.23	4.16	3.6	2.0	880
R1	3.35	5.11	4.0	3.6	1010
R2	3.35	4.59	4.0	2.9	1220

Table 7b
pH, acidity and substances of low molecular weight for the red musts (from *Tinta de Toro* grapes). Note that some items have not been measured for P1 because they were considered irrelevant for our purposes.

Must	pH	A.T. (g/L)	MH2 (g/L)	TH2 (g/L)	SO_2L (mg/L)	SO_2T (mg/L)	Potassium (mg/L)
T	3.76	3.78	3.8	2.1	29	51	1820
P1	3.75	3.45	3.7	1.6			1700
P2	3.75	3.45	3.8	1.5	3	20	1630
R1	3.74	3.80	3.8	1.9	30	72	1920
R2	3.75	3.57	3.4	2.2	8	40	1720

these retentions as percentages. It is noted that whereas in the first stage the sugar retention is similar for white and red musts, in the second process, in the total one and also by comparing with the control must, the sugar reduction is more significant in the case of red musts. This was to be expected due to the presence of higher amounts of colloidal substances in red musts. These stick on to the membrane surface and form a pseudo-membrane which adds its own retention capacity to that of the actual membrane.

Tables 7a and 7b show the results of the analysis of other relevant low molecular weight substances. The general trend is a slight decrease of these substance in the permeates and an increase in the retentates. But these variations are too small for most of these compounds. Therefore, they should be much less important in the onset of the osmotic pressure gradient than sugars.

The retention of these substances should also be related with their molecular weight and with their charge, because the HL membrane has an isoelectric point of 3.3 [34] and the membrane is negatively charged at pH of the musts (see Table 1). This explains the ion retention, as for potassium despite its low molecular weight (MW = 39.1 g/mol). In the case of the malic acid (MW = 134.09 g/mol, pK = 3.40), variations are more associated to the error of the calculation method than to the filtration process. However, tartaric acid (MW = 150 g/mol, pK = 3.03) with only slightly higher molecular weight and lower pK (higher ionization) is more retained than malic acid.

In the case of SO_2 (MW = 64.1 g/mol) for red musts, where it was added to the must to prevent oxidation and as antiseptic among other functions, it can be seen that there is a high retention (see Table 7b) of the free SO_2. This must be due to the formation of sulfurous acid that should be strongly dissociated and thus retained by a charge mechanism. Other possible reason for the low content of SO_2 in the permeates could be its elimination due to evaporation because it is highly volatile. Many of these substances are also associated with others of a higher molecular weight, in that way they are retained by the membrane despite its small size.

The phenolic compounds are mainly related to the color of wine and have higher molecular weights than sugars. Due to their size, they present a high retention, which will force to recover these substances for the final wine by mixing the permeate (P2) with the initial retentate (R1) or the control wine (T) in order to avoid arriving to a unbalanced wine. In that way we can recover the levels of total polyphenols, catechins, tartaric esters and flavonols than the control white must had initially. As shown in Fig. 4a and b, these compounds are retained mainly during the initial filtering phase.

Taking into account the volumes of the solution filtrated (Table 2), the last permeate (P2) and the initial retentate (R1) have the highest volume. The first permeate (P1) has an intermediate volume and it is filtered again; and, the only solution whose compounds are never entering the final wine is the retentate of the second filtration (R2). Table 8 shows the total volume of must lost when the P2 + T and P2 + R1 blendings are done. It is worth noting that the two-step nanofiltration step was not designed by taking into account the efficiency in volume of the process for the P2 + T mixture but rather with the P2 + R1 in main. This is why the volume loss resulted relatively high. An optimization of the details of the process should eventually optimize these volume losses.

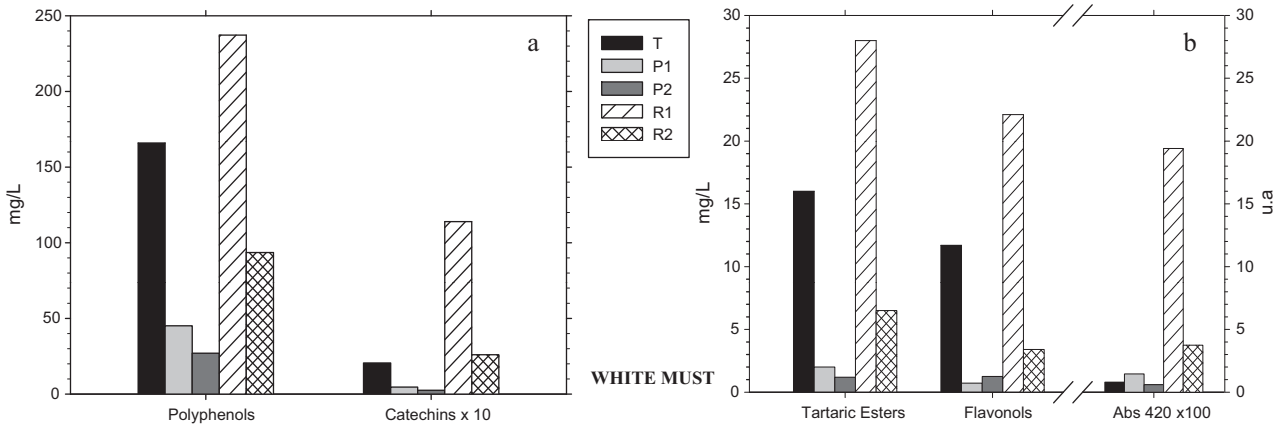

Fig. 4. Concentration of the compounds related with the color and absorbance at 420 for the control must and the other different mixtures of the white must filtrated (a) polyphenols, catechins, (b) tartaric esters, flavonols and Abs 420 absorbance at 420 nm.

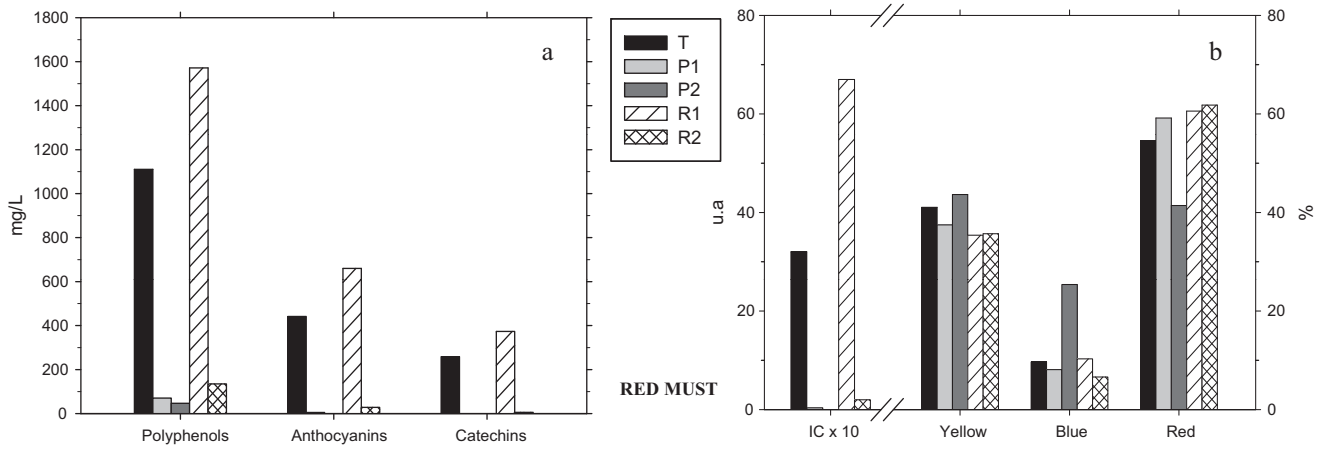

Fig. 5. Concentration of the compounds related with the color of the control must and the other different mixtures of the red must filtrated. (a) Phenolic analysis musts, (b) IC: Color index (defined as the addition of absorbances at 420 nm, 520 nm and 620 nm) and percentage of the three fundamental colors.

Table 8
Lost volume for the must in the nanofiltration process.

	% volume white must lost	% volume red must lost
P2 + T	45.0	50.0
P2 + R1	6.7	6.7

The relation between the concentration in the retentate (R1) and that in the permeate (P2) is about 10 for total polyphenols and flavonols, and a somewhat higher, about 30, for catechins and the tartaric esters. The analysis of absorbance at 420 nm (mainly responsible for the color of white musts) has a difficult to interpret behavior. In any case, the relation R1/P2 is approximately 32 which is similar to that for the concentrations of catechins which seems to indicate that catechins should be mainly responsible for the color formation with less influence of the other polyphenols and flavonols. On the other hand, the permeates have a color index close or even higher (this is the case for P1) than that of the control wine. This increase in the base color level indicates that it is not only controlled by catechins and flavonols. The observed general slight increase of color should be due to some oxidation during the filtration steps (mainly during the first filtration step).

Fig. 5a presents the results of the process for total polyphenols, anthocyanins and catechins for red musts (*Tinta de Toro*). The relation R1/P2 is approximately 30 for polyphenols, about 200 for the catechins and more than 5000 for the anthocyanins. In this case the retention is much higher than for white musts, due to the big number of substances and their high concentration in red musts. Retention of total polyphenols is almost 7 times higher for red musts than for white musts while the ratio for catechins is almost 33.

Fig. 5b shows the results of the color analysis for the red must. There is a strong reduction in the color index, due to the high molecular weight of the substances giving the color to the red must. These substances have a strong colloidal character, which keeps facilitating their aggregation [42]. If we analyze the variation of fundamental colors, they clearly show a reduction of the red intensity in P2 and an increase in R1 when compared with the control must T, with opposite tendencies for both the yellow and the blue components. This increase for the yellow component in P2 is possibly due to some oxidation appearing during filtration as already noted with white musts.

3.3. Production and analysis of wines

Several wines have been produced with the white and red musts. In the case of the white must, the following wines were made in order to assess the quality of the final wines with reduced alcohol content:

- Control wine made from the control must (T).
- Low alcohol content wine 1 obtained from the control must T plus the nanofiltered permeate P2 in proportions intended in order to reduce the probable alcohol content by approximately 2°. (T + P2).
- Low alcohol content wine 2 made from the nanofilter permeate P2 plus the retentate of the first nanofiltration step R1. Here the intended alcohol reduction is also of approximately 2° (R1 + P2).
- Retentate wine 1 obtained from the fermentation of the nanofiltered retentate (R1).
- Retentate wine 2 obtained from the full fermentation of the nanofilter retentate (R2).

All the experiments were carried out in duplicate in 4-L tanks. In all cases fermentation was initiated by the inoculation commercial yeast and at a controlled temperature. Once the alcoholic fermentation was completed the wines were racked, bottled and stored for their later analysis.

Table 9 shows the results for the analysis of the white wines made by us. After alcoholic fermentation, wines T + P2 and R1 + P2 had an alcohol content decreased by 2.5° and 3.3° (v/v), respectively, when compared with that of the control wine T. In both cases

Table 9
Classical oenological parameters of the white wines after alcoholic fermentation.

Operation	pH	A.T. (g/L)	A.V. (g/L)	MH2 (g/L)	TH2 (g/L)	Sugar (g/L)	Alcoholic degree %vol	Potassium (mg/L)
T	3.05	7.42	0.21	2.9	2.8	1.65	12.71	675
T + P2	3.08	7.78	0.13	2.9	4.1	1.64	10.14	945
R1 + P2	3.06	7.78	0.13	2.8	4.2	1.66	9.34	915
R1	3.14	7.43	0.35	2.7	2.8	2.12	16.82	660
R2	3.07	8.17	0.18	2.7	2.3	1.77	13.71	790

A.V. = volatile acidity.

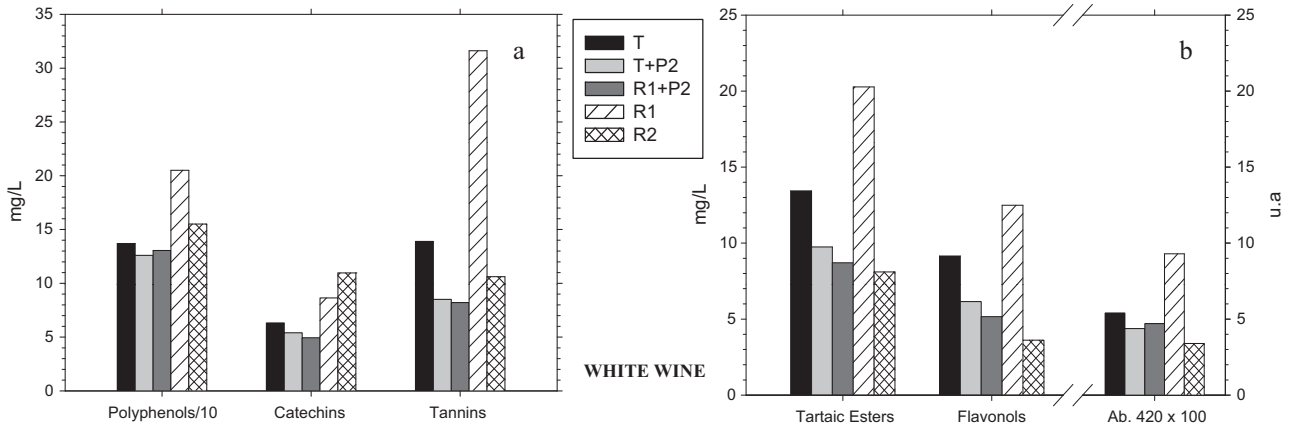

Fig. 6. Concentration of the compounds related with the color and absorbance at 420 for the control and the other white wines (a) polyphenols, catechins, (b) tartaric esters, flavonols and Abs 420 absorbance at 420 nm.

the reduction achieved was higher than the 2° initially anticipated, this difference is attributable to the difficulty involved in determining the exact proportions of musts to blend. It is worth noting that these wines with reduced alcohol content had higher levels of tartaric acid and potassium than the other wines produced, probably due to the fact that in the wines with high alcoholic degree, the reaction of tartaric acid with potassium is favored giving potassium bitartrate that precipitates [28] (Table 9). In the case of the other oenological parameters studied, no significant differences were found between the various wines elaborated.

Fig. 6a and b show the concentrations of polyphenols and other compounds related with color for each of the wines produced. There is a very weak decrease of total polyphenols and color index at 420 nm in the reduced degree wines compared with the control wine. Nevertheless, a slightly higher decrease appears for some specific compounds such as tannins. As logically it should be expected that in R1 there is an accumulation of these substances.

A similar process was used for the making of the *Tinta de Toro* wines, but in this case the must was not blended prior to be fermented but they were fermented separately and later brought together to obtain a wine with the desired alcohol content. A 40% of the crushed mass was added to the T, R1 and P2 musts and then fermented. Each of these musts was fermented by duplicate in 35-L tanks. Once the alcoholic fermentation was completed, the wines were racked. Next, and in accordance with their alcohol content, they were mixed. The following wines were produced:

- Control wine (T).
- Low alcohol content wine 1 made by mixing the control wine with an adequate amount of the wine obtained from the fermentation of the nanofiltration permeate to get a reduction in the alcohol content in approximately 2° (T + P2).
- Low alcohol content wine 2 obtained by combining the fermented retentate resulting after the first filtration step R1 and the corresponding part of the wine obtained from the fermentation of the final permeate P2. The intended reduction in the alcoholic content was also approximately 2° (R1 + P2).
- Once the wines were blended, the next stage was the malolactic fermentation, after which the wines were racked and bottled for analysis.

The results obtained for the oenological parameters for the red wine, after alcoholic fermentation, were similar to those obtained for the white wines. This means that the filtering process only retained reducing sugars while allowing malic and tartaric acids and potassium to pass (Table 10a). Therefore the only difference clearly detectable is the alcoholic degree. This difference in the alcohol graduation remains as the single singularizing factor after the malolactic fermentation (Table 10b).

Nanofiltration clearly did not allow the phenolic compounds to pass freely to the permeate. In effect, polyphenols, anthocyanins, catechins and tannins – all large compounds – are relatively scarce in P2 and consequently their concentrations increased in R1, as was already commented referring to the red musts. Red wines have also been analyzed to know the changes in the concentrations of these large molecules as shown in Fig. 7a. Moreover the proportions of anthocyanins in monomeric or polymeric forms and the amount of copigments in presence have also been studied and shown in Fig. 7b. As expected, the largest molecules are more abundant in

Table 10a
Classical oenological parameters for the control wine and the different products of filtration and mixtures after alcoholic fermentation for red musts (*Tinta de Toro*). Note that some items have not been measured for P2 and R1 because they were considered irrelevant for our purposes.

Wine	pH	A.T. (g/L)	A.V. (g/L)	MH2 (g/L)	TH2 (g/L)	Sugar (g/L)	Alcoholic degree %vol	Potassium (mg/L)
T	3.69	6.58	0.55	3.2	3.6	1.50	14.82	1760
P2	3.64	5.86	–	–	–	–	7.82	–
R1	3.80	6.29	–	–	–	–	17.54	–
T + P2	3.70	6.73	0.46	3.3	3.6	1.30	12.96	1730
R1 + P2	3.70	6.02	0.41	3.3	3.7	1.30	12.73	1630

Table 10b
Classical oenological parameters for the control wine and the different products of filtration and mixtures after malolactic for red musts (*Tinta de Toro*).

Wine	pH	A.T. (g/L)	A.V. (g/L)	MH2 (g/L)	TH2 (g/L)	Sugar (g/L)	Alcoholic degree %vol	Potassium (mg/L)
T	3.89	5.05	0.65	0.10	1.17	1.30	14.28	1555
T + P2	3.88	4.69	0.57	0.10	0.98	1.30	12.49	1435
R1 + P2	3.87	4.16	0.52	0.10	0.94	1.30	12.47	1380

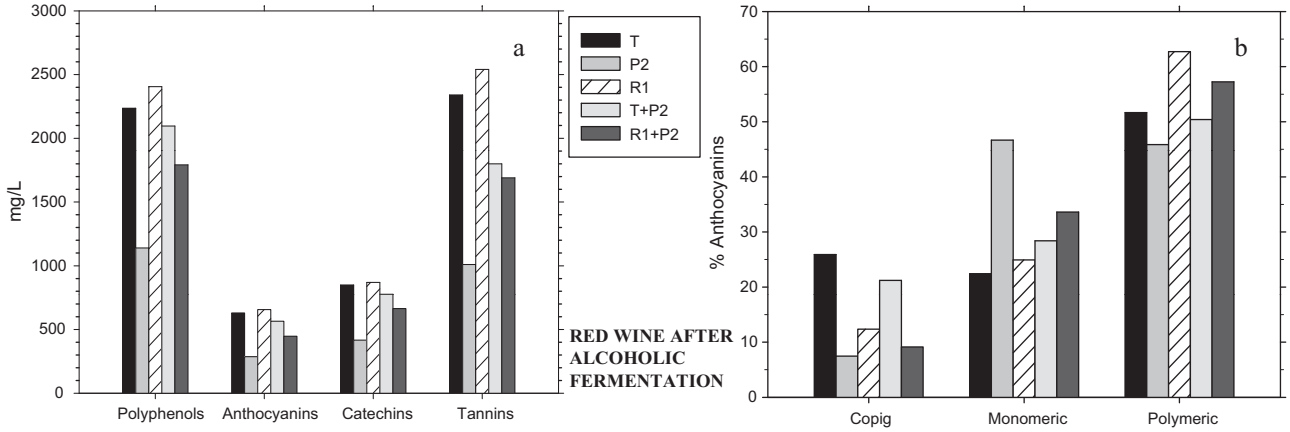

Fig. 7. Concentration of the compounds related with the color of the control and other red wines after alcoholic fermentation. (a) Phenols and (b) % Anthocyanins.

the wines obtained from the retentate and the smallest ones in the wines made from the permeates. The low content of copigments and the high content of monomer suggest a possible rupture of the copigments molecules during the nanofiltration process. In any case it seems clear that the T + P2 appears as the most similar to the control red wine in concentrations of large molecules and also attending to the different fractions of anthocyanins.

After the malolactic fermentation, these compounds have been also studied along with the tartaric esters and flavonols (Fig. 8a and b). The final wines with a decreased alcohol content also revealed lower concentrations of phenolic compounds than those in the control wine. This loss of phenolic compounds during nanofiltration led to a significant reduction in color intensity. This was particularly noticeable in the case of wine R1 + P2. In the case of wine T + P2 these differences were less than 12% of the total polyphenols, anthocyanins and catechins. Although the color of this wine was less intense than the control wine, the tone and percentages of blue, yellow and red were similar (Fig. 8c).

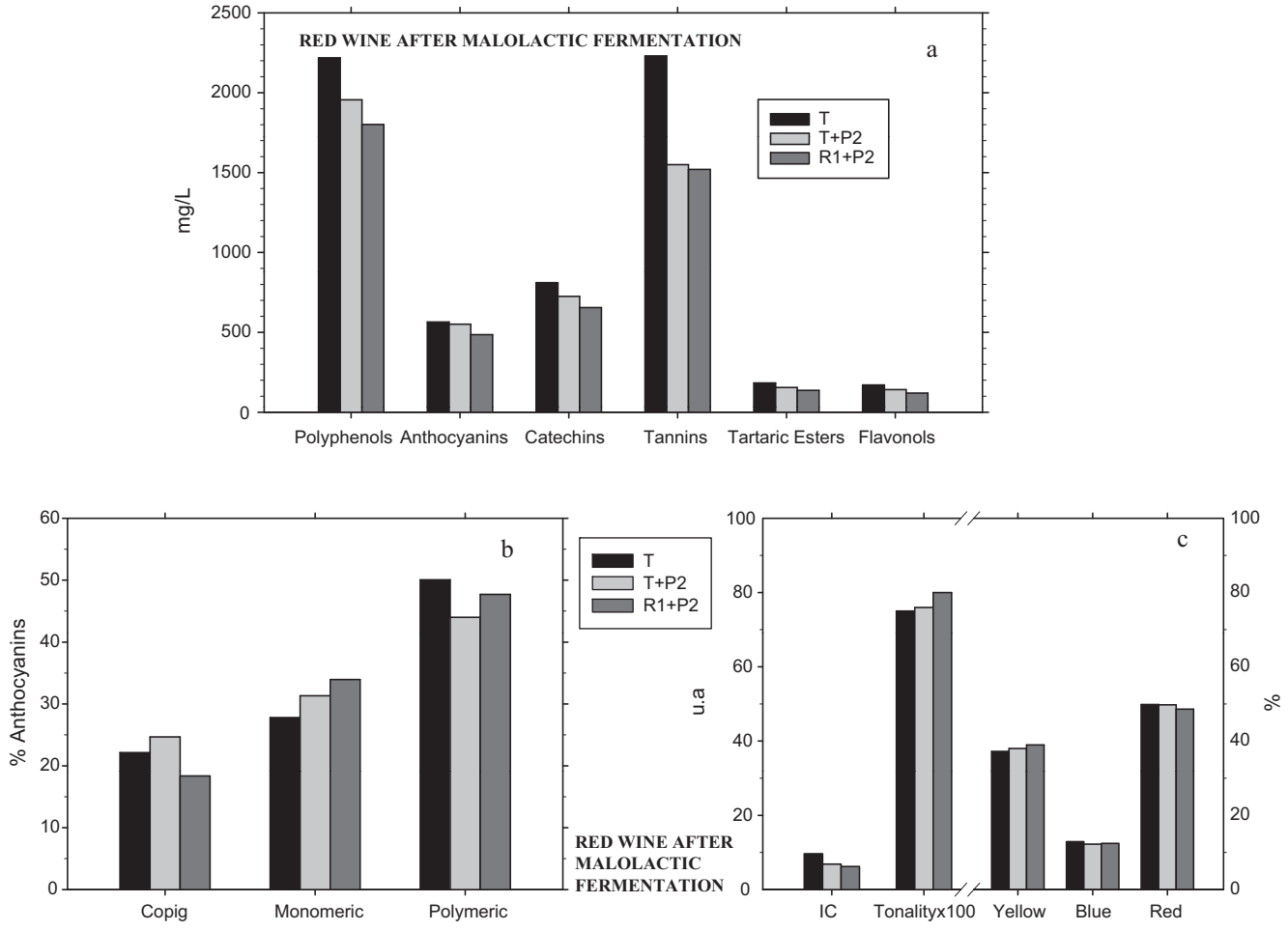

Fig. 8. Concentration of the compounds related with the color of the control and other red wines after malolactic fermentation: (a) polyphenols, anthocyanins, catechins, tannins, tartaric esters and flavonols, (b) % anthocyanins, (c) IC: Color index, tonality and percentage of the fundamental colors.

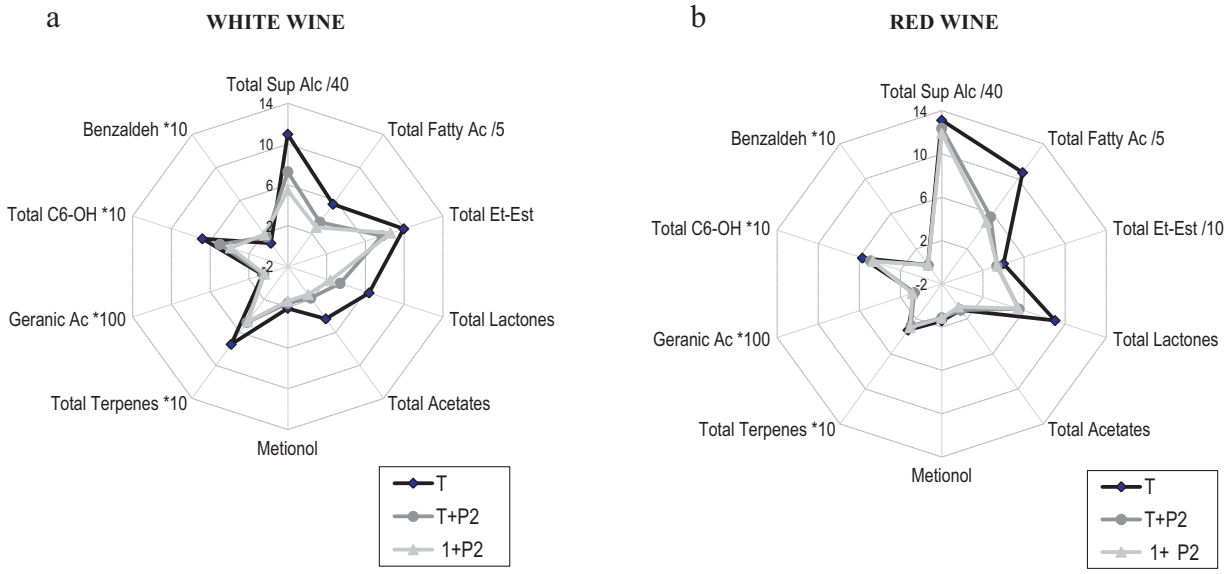

Fig. 9. Concentration in mg/L of the different families of volatile compounds present in the control wine and in the reduced alcohol wines: (a) white wines and (b) red wines.

The volatile fraction was also analyzed in order to help the study of the organoleptic properties of the final white and red wines. Because a great amount of volatile compounds were identified, the results have been analyzed after grouping the quantified volatile compounds in a few relevant classes. The compounds were grouped according to chemical similarities. The following groups were formed:

- Ethyl esters (Total Et-Est): ethyl-butyrate, isovalerate, hexanoate, octanoate, decanoate, and lactate; di-ethyl succinate and glutarate; and ethyl-3-hydroxybutyrate.
- Fusel alcohol or Superior alcohols and benzyl alcohol (Total Sup Alc): butanol, isobutanol, pentanol, isopentanol, heptanol, octanol, 2-phenyl-ethanol and benzyl alcohol.
- Acetates (Acetates): isoamyl-acetate, hexyl acetate, and phenylethyl acetate.
- Fatty acids and succinic acid (Total Fatty Ac): succinic, pentanoic, isopentanoic, hexanoic, octanoic, decanoic and dodecanoic acids.
- Lactones (Total Lactones): γ-Butyrolactone and γ-nanolactone.
- C6 alcohols (Total C6-OH): hexanol and cis and trans-3-hexen-ol.
- Terpenic compounds (Total Terpenes): α-terpineol, citronellol, geraniol, linalool, nerol, and β-ionone.
- Benzaldehyde.
- Methionol and
- Geranic acid.

The volatile profile of control white wines (T) was largely different from that of the wines obtained after modifying the sugar levels of the must (T + P2 and R1 + P2). These wines were very similar between them (Fig. 9a). Important differences were found for all the studied compounds between the control wine and the reduced alcohol wines being the control wines richer in volatile compounds than the rest of the wines. Quantitative important differences in the levels of fusel alcohols, fatty acids, ethyl-esters, lactones, acetates and terpenoids were observed. On the other hand, the level of benzaldehyde detected in control wines was lower than in the rest of the wines. These results could be linked to the lack of sugars in the "modified musts", this should lead to a less intense fermentation process with a lower production of fermentation volatiles. Regarding terpenic compounds, some low levels of terpenes could be found in grapes, however in the fruit are predominant the odorless forms (glycosides structures) known as precursors. They are hydrolyzed during the alcoholic fermentation by enzymatic action of the yeast, increasing the levels of terpenes in wines (respect to the must). So, a more intense fermentation process should enhance a more efficient hydrolysis leading to a higher formation of these compounds. Furthermore, the precursors could be eliminated during the NF process of the must, specially during the first step, remaining in the retentates.

The results for the volatile compounds of the products obtained by fermentation of the retentates R1 and R2, which are not shown, gave volatile profiles that were different from those for the elaborated wines, being in general richer in volatile compounds. R2 resulted was especially rich in lactones and R1 was principally rich in terpenic compounds. This fact is associated and corroborated with the comments about the retention of the precursors in the retentate of the first NF step. The products obtained after fermentation of retentates were judged as intense odorant products, reasonably balanced in the tasting analysis.

In the case of red wines (Fig. 9b), the most important differences are found in fatty acids, ethyl-esters and lactones. As in the previous situation, this behavior may be due to the combination of a number of factors associated with the low sugar levels in the musts and the retention of substances during NF treatment.

These results agree with the taster's comments who indicated that control wines showed more intense aroma, with higher floral and fruity notes, whereas the wines elaborated with filtered musts were less intense in the olfactory phase. In effect

- The sensorial analysis of the elaborated white wines with reduced alcohol content revealed no defects in terms of their color or olfactory qualities. Indeed, no differences were observed between the color of the control wine and those with a reduced alcohol content. On the nose, the control wine displayed a greater aromatic intensity when compared to those wines with reduced alcohol content. As should be expected, the greatest variations were detected during the tasting phase, as the reduction in the alcohol level modifies the taste perception of the other compounds present in the wine. The wines with a reduced alcohol content were described by the tasters as being more acidic and lighter than the control wine, especially wine R1 + P2, maybe because its alcohol content resulted to be slightly lower than for T + P2.
- In the sensorial analysis of red wines, no differences in color were found, although variations were observed during the olfactory

phase. The aroma of wine T + P2 was less intense than the control wine, whilst artificial pharmacy/chemist aromas were detected in the case of the R1 + P2 wine. In the mouth, the only differences detected between the control wine and the wines with reduced alcohol content consisted in the gustative translation of this olfactory observation.

4. Conclusions

As an answer to the modern trends towards healthy lifestyles and reduced calorie intake, a new method to obtain low-alcohol wines is proposed here. The advantage of this method is to work with musts, instead of manipulating the wines. This should make easier to preserve the organoleptic properties resulting from fermentation. In view of the results and their comparison for the untreated wines and the newly obtained, we consider that the product, especially T + P2, exhibits good results. Until now one of the problems was the no completely satisfactory sensory quality of the lower-alcohol wines. Attending to the results obtained in terms of aroma and taste, it seems appropriate to try to reduce the filtration time, for example by increasing the membrane area or maybe the applied pressure. An increase in the tangential velocity should be dangerous as could increase oxidation of the musts. It should be also interesting to work in an inert atmosphere in order to reduce the loss of flavor and prevent possible oxidation of some compounds.

Concerning the flux decay detected, it cannot be avoided because musts are really complex liquids with extreme colloidal and fouling properties. Nevertheless, the extent of the decay allows a relatively long-term stability and recovery after cleaning that permitted adequate nanofiltration.

Obviously, the success of the method depends on the characteristics of the wine as an answer to the demanded product; and on the production cost, which is a critical factor in the viability. This method is inexpensive in terms of production costs and although it leads to a loss of volume of the must, the profitability of the process can be increased using the retained portion R2 for the production of sweet wines, liquors or additives for functional foods.

Acknowledgements

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